ASSOCIATION OF ACETIC ACID IN NON-AQUEOUS SOLVENTS*

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Plate XI

ABSTRACT. After a review of the work on acetic acid in water, the necessity for the study of this substance in non-aqueous solvents is stressed. Investigations were made with both polar and non polar liquids as solvents for this acid. The changes in Raman frequencies of this liquid in mixtures with chloroform, nitrobenzene, ethyl ether, acetone and methyl-ethyl ketone are described. No changes are perceptible in solutions with chloroform. This is explained on the basis of the absence of either a donor or an acceptor atom in this solvent, which is therefore supposed not to have any influence on the acid. The other four substances, on the other hand, bring about distinct shifts in the C = O frequency in particular. This is attributed to the presence of the donor atom O in these molecules, which is in a position to associate with the acceptor H in the acid molecules. Such an association can bring about the splitting of the associated molecules of the acid also, which therefore results in the change of the Raman frequencies of the acid. A new line with frequency 1760 cm^{-1} is ascribed to the free C = O bond in the acid which arises out of the disruption of the acid complexes into simpler molecules and which remains free in the new complex formed with the solvent, as there is no acceptor H in the molecules of these solvents to get associated with the O in it.

INTRODUCTION

In a previous publication,[1] the author studied the Raman spectrum of acetic acid at different concentrations in water and found that the principal C=O band of the acid with its intensity maximum at 1670 gradually shifted with dilution towards higher frequencies. At 25% concentration of the acid, it was found that the intensity maximum of the C=O band was about 1710. By a study of the effect of temperature on the acid, it was found that by increasing the temperature the intensity maximum again shifted in the same direction. It was pointed out that the appearance of the band at 100° C in the pure acid was similar to that at 95% concentration of the acid in water. These results were attributed to the breaking up of the initially associated molecules of the acid into lower polymers at higher temperatures and at higher dilutions. Similar results obtained with formic and benzoic acids in aqueous solutions were explained similarly.[2,3]

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While these changes were observed in aqueous solutions, the acid showed no change in solvents like benzene and carbon-tetra chloride. The two non-aqueous solvents chosen having been non-polar, the dissociating effect in aqueous solutions was attributed to the polar solvent, water.

A further elucidation of the phenomenon was necessary for a complete understanding of the phenomenon of association in acetic acid and hence the author studied the Raman spectrum of the acid in other non-aqueous polar solvents. The results obtained are detailed below.

EXPERIMENTAL

The usual experimental arrangements for obtaining Raman spectra of liquids described already in the author's previous communication[1] were used. The liquids under study were distilled in vacuum and rendered free from water to eliminate its effect. Transferring of solutions was done without disturbing the arrangement. Thus the slit of the spectrograph was kept at the same constant width throughout the investigations.

RESULTS

Polar liquids can be broadly classified as normal and abnormal. Among these, normal liquids are those, which, though polar, are not associated. Abnormal liquids are highly associated and show abnormal physico-chemical properties. The fatty acids, alcohols and water are prominent examples of abnormal liquids, while almost all other polar liquids are normal—acetone, ether, nitrobenzene, etc. But some of these normal liquids have got a strong tendency to associate with other molecules. A molecule having a 'donor' atom has got affinity for one having an 'acceptor' atom and forms a donor-acceptor link with it. An associated liquid has got both a donor and an acceptor and hence co-ordination or hydrogen bond formation (as the American school calls it) takes place and the molecules associate.

The effect of chloroform, nitrobenzene, diethyl-ether, acetone, and methyl-ethyl ketone on acetic acid was studied with a view to observe the changes in the polymerisation of the acid. Of these, nitrobenzene has the highest dipole-moment about 4×10^{-18} e.s.u. and the rest of the solvents have moments ranging from 1·55 for ether to 2·5 for acetone.

The following results were obtained : the first three solutions were 50 : 50 mixtures by volume.

1. *Solution in chloroform.*

There are no prominent changes in the Raman lines of acetic acid in chloroform.

In Nitrobenzene.

The C – C line of acetic acid at $\Delta\nu = 893$ is unchanged. The C = O line at 1670 rendered less diffuse and another line at about 1760 makes its appearance. Both these lines are not very clear on the plate due to the continuous spectrum which developed during the exposure.

3. *In Ether.*

The C – C line in the pure acid has a faint component at about 872, which is not visible with ordinary exposures. In the solution in ether, this line accompanying the 893-line increases in intensity such that it is clearly seen, comparable in intensity to the strongest 893-line. The C = O line at 1670 gets more diffuse than in the pure acid and two diffuse lines, with intensity maxima at 1685 and 1750 can be clearly seen.

4. *In Acetone.*

The most prominent changes are undergone by acetic acid in mixtures of acetone and of methyl-ethyl ketone with the acid. Three different concentrations, 75%, 50%, and 25% of the acid in the mixture have been studied.

Conspicuous changes are observed on the following lines :

C – C line.—As in the case of solution in ether, the low-frequency companion at 872 makes its appearance in a 75% solution, and as the concentration of the acid in the mixture decreases, the low-frequency component increases in intensity, till at 25% concentration, it is more intense than the 893-line itself. There is no line in acetone in that region and hence the effect can be attributed only to acetic acid molecules (Fig. 1) (Plate XI). In the microphotomeric curves given in fig. 1 the increase in intensity of the 872-line at higher concentrations is clearly seen.

C = O line.—In pure acetic acid, the C = O frequency is about 1670. In pure acetone it is about 1712. In the mixture the 1670-line maximum is seen proceeding towards higher frequencies with dilution till it gets blended with the acetone line. In addition, a line at 1760 which is quite sharp, makes its appearance. This line is present at all the three concentrations studied.

$\Delta\nu = 623$.

This line also seems to change in a manner similar to the C – C line at 893. In the pure acid, it has got a low-frequency component at 601, but the component is too feeble to be visible with ordinary exposures. But as the concentration of acetic acid in the mixture decreases, the intensity of its low-frequency component increases correspondingly.

5. *In Methyl-ethyl ketone.*

The effect in methyl-ethyl ketone is similar to that in acetone. As before, there is a clear splitting of the 893-line and an increase in the intensity of its low-

frequency component with increasing dilution of the acid in the solvent (Fig. 1). The line at 1670 shifts towards higher frequencies till it gets blended with the C=O line of the ketone at 1715 and the new line at 1760 also makes its appearance. The effect on the line 623 could not be studied due to the presence of another ketone line close to it.

Comparison of these results with those obtained by dilution in other Solvents.

For a proper understanding of the behaviour of acetic acid molecules in the different solvents studied, a comparison of the results obtained with other solvents also is necessary. We shall first take the C=O line at 1670 which is bound to be affected most by polymerisation or depolymerisation.

In non-polar solvents, benzene and carbon-tetrachloride, this line is unaffected. Among other solvents, chloroform does not seem to have any perceptible effect on it. Nitrobenzene splits it into two components, one at 1670 and another at 1760. The same is the case with ether but the 1670-line shifts slightly towards higher frequencies and both the lines are very diffuse unlike what they are in nitrobenzene solution. In ketones (acetone and methyl-ethyl ketone) as solvents, we again see the 1670-line shifting towards higher frequencies and the 1760-line appearing. The actual position of the shifted 1670-line and its spectral characteristics cannot be estimated on account of the superposition of the 1715-line of the ketone on it. While in all these polar solvents, a clear distinct line at 1760 is obtained, it is significant that in water alone, no such line at 1760 is found even at a dilution of 25%. In aqueous solutions, the 1760-line gets more and more diffuse and shifts gradually towards higher frequencies.[2] At no stage can two distinct lines, either sharp and separate as in nitrobenzene or diffuse and yet discreet as in ether, be obtained.

With regard to other lines, there is again a difference in their behaviour in water and in the other polar solvents. The 620- and 893-lines are unaffected in solutions in non-polar solvents and in chloroform In nitrobenzene there does not seem to be any conspicuous change. But in ether both of them double up with low-frequency components at 601 and 872 respectively. In acetone and methyl-ethyl ketone, the same is the case and we find that as the concentration of the acid in the solution diminishes, the low-frequency lines become more intense till at 25% acid in acetone, the 872-line outshines its companion. The reverse happens in aqueous solutions The lines tend to become more diffuse with decreasing concentration, the low-frequency component disappearing even at high concentrations. This is again a conspicuous difference between aqueous and non-aqueous solutions of the polar type.

DISCUSSION

To understand the changes listed above, we must first get an idea of the molecular structure of the acid and that of the solvent used. As we already know,

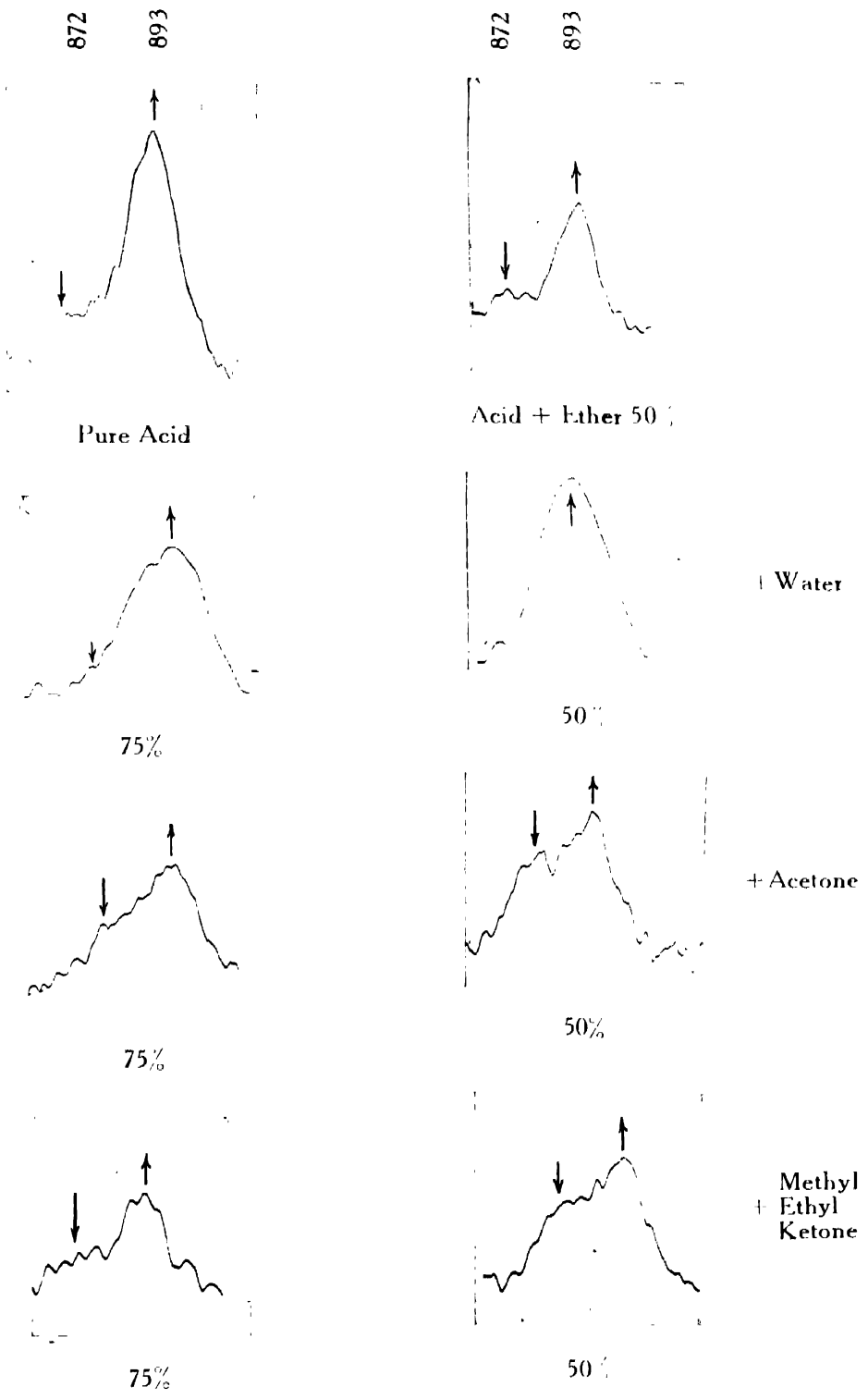
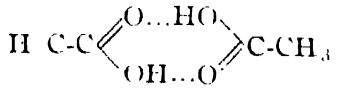


Fig. 1. C-C Lines of Acetic Acid in different Solvents

the acid is an associated liquid, mostly containing dimers of the type



There is no definite evidence for the existence or non-existence of other more complicated molecules or less complicated ones. The solvents employed in these investigations are of three types: (1) non-polar, (2) polar and normal and (3) polar and abnormal or associated. In the first case no changes are observed, showing that the acid molecules remain as they are This observation is in consonance with existing physico-chemical data which gives abnormal values for the molecular weights of acetic acid in non-polar solvents like benzene.

In polar solvents, changes are observed, showing thereby that the molecular structure of the acid is affected. The following changes may take place :

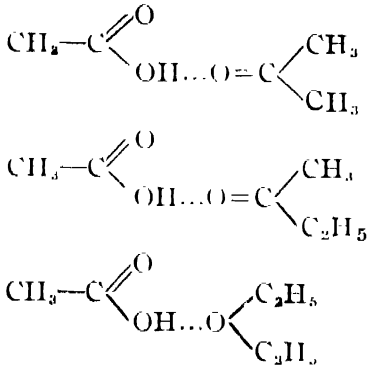
(*i*) Breaking up of associated molecules into simpler ones.

(*ii*) Formation of complexes between the solvent molecules and the simple molecules so liberated.

Thus, in general, there is the possibility of such a solution containing the following types of molecules : (I) unbroken molecular aggregates of the pure acid, (II), lower polymers like monomers and (III) complexes formed with the solvent. An explanation of the changes observed in the Raman spectrum of the acid in the different polar solvents is bound to be dependent upon the factors outlined above.

Next we should consider the effect of these changes upon the frequencies of the particular oscillations studied. The author has already pointed out that the effect of association on the C=O line is to reduce its frequency and the effect of depolymerisation is to increase it, if the co-ordination or the formation of the hydrogen bond takes place on the O in C=O.[1,2,3] Based upon this factor, it was argued that in aqueous solutions of acetic, formic and benzoic acids, the increase in frequency of the C=O band is due to the formation of lower polymers. Association can take place not only through the O in C=O, but through H in OH which can act as an acceptor. It is only in the case of similar molecules, *i.e.*, in the case of molecular polymers of the pure acid alone, that both the donor and acceptor atoms are linked up through hydrogen bonds. If, on the other hand, a different molecule, say ether or acetone, forms a complex with the acid, then its donor atoms link up only with the acceptor atoms in the acid, *viz.*, with the H in OH. Thus, the C=O is unlinked, its external binding through the hydrogen bond is released, and the effect on it, if any, of the hydrogen bond at the end of the H in OH may not be towards diminishing it. Hence, again, there is an increase in the frequency of the C=O, if a molecular complex is formed between the acid molecule and another molecule having a donor atom.

The changes undergone by the Raman lines of acetone and methyl-ethyl ketone in acetic acid are discussed in another paper.[5] The effect of acetone, methyl-ethyl ketone and ether on the acid seems to be to break up the associated molecules (probably dimers) into their monomers and form complexes with them of the types



In all these, the C=O linkage of the acid is unattached and hence the 1760-line may probably be due to this. That it may not be due to the C=O in acetone or methyl-ethyl ketone is shown by the fact that the line is present in solutions in ether as well as in nitrobenzene.

The C–C binding in these cases seems to be affected by the formation of these complexes. Hence the appearance of the new line at 872. The fact that the line increases in intensity with increasing dilution of the acid shows that at greater dilutions more and more molecules of the acid are broken up and link themselves to the solvent to form complexes. The changes in the 620-line are explained similarly. The author attributed[1] this line to an external oscillation of the carboxyl group. If this group is attached to an external molecule, the line is bound to be displaced and the doubling is caused by the presence of attached and unattached molecules in the mixture. Further confirmation of this is found in the fact that these low-frequency components appear in the pure state of the acid, while they disappear at greater dilutions in water. The fact that the 893-line is not doubled in solutions of acetic acid in nitrobenzene is probably due to the non-formation of complexes. The effect of nitrobenzene may be merely to break up the dimers into monomers on account of its large dipole moment. The NO_2-line of nitrobenzene is itself unshifted and hence this conjecture. Chloroform does not seem to have any effect at all on the acid. Probably the effect of the dipole interaction is too feeble to break the dimers of the acid.

The effect of water on the acid is distinctly dissimilar to that of all the previous solvents studied. While there is the appearance of two distinct lines for the frequencies 620, 893 and 1670 in all the other polar solvents, in water there is a gradual shifting of the maximum of the 1670-band towards 1710 at higher dilutions and the other lines merely get diffuse, the low-frequency compo-

nents disappearing. This, as has been already pointed out, seems to be due to the breaking up of the higher polymers into lower ones. The fact that the low-frequency components of the 620- and 893-lines which are characteristic of the higher polymers disappear in aqueous solutions, lends support to this view. But it may be argued, why don't water molecules link themselves up with the monomers so formed and form complexes as in the case of solutions in acetone and methyl-ethyl ketone? If they should link up to the C=O, the C=O frequency must be diminished. But in fact it increases. The lines characteristic of the higher polymers of the complexes formed with the monomers, *viz.*, the low-frequency components of the 620- and 893-lines are absent in aqueous solution. Hence it is evident from the data that hydrates with water do not seem to be formed. There is another way of linking in order to form a hydrate. The H in OH in acetic acid may act as an acceptor and the O in water may be the donor. Then the structure of the hydrate resembles that of the acetonate given already and hence the 1760-line must be expected. Also the low-frequency components of the lines 620 and 893 must make their appearance as in the case of other solvents. Experiment shows that there is no trace of a separate and distinct 1760-line and that the 601- and 872-lines actually disappear in aqueous solutions. Moreover, physico-chemical data of Jones and his co-workers point out to the non-existence of hydrates of acetic acid in aqueous solutions.[4] Hence the changes of the Raman lines of acetic acid in aqueous solutions seem to be due only to a depolymerisation of the acid in the solvent, as pointed out elsewhere.[5]

Probably a distinction can be drawn between the effect of other polar solvents and that of water. In the case of water, we are treating with an abnormal and associated liquid. It is well known that the effect of one associated liquid on another is towards mutual depolymerisation. Each tends to diminish the association of the other. Probably that is so in mixtures of fatty acids and water.

The extreme diffuseness not only of the C=O line but of every other line in aqueous solutions appears to be due to the fluctuations of the polarisation field of the water envelope round each molecule in general. The effect of this field and its fluctuations is maximum in the case of water as compared to the other polar solvents, probably on account of the small size of the molecule.

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